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Al_2O_3–SiO_2 CERAMIC MATERIALS FOR ELECTROVACUUM GLASS WELDS IN THE GLASS ELECTRODES OF pH-METERS

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The results of research on obtaining Al_2O_3–SiO_2 based electric-insulation ceramic materials using ceramic mixes containing fireclay as a plastic component and silica-containing materials — crystalline quartz (quartz sand) and amorphous silicon (silica-gel) — to secure the required properties are presented.

Key words: electrolytic key, weld, CLTE, porous structure, high-silica ceramic, quartz, amorphous silica.

Glass electrodes surpass all other electrodes in convenience and versatility, and more recently they have monopoly on pH measurements and regulation in scientific research and industry. A glass electrode is distinguished from other indicator pH electrodes by its reliability, high measurement accuracy and stability against chemical actions, including by strong oxidizing and reducing agents [1].

In the Republic of Belarus the main manufacturer and supplier of glass electrodes for pH measuring instruments is the Republic Unitary Enterprise Gomel' Instrumentation Works (GZIP). This enterprise manufactures a wide assortment of glass electrodes: laboratory (four types), about 7000/yr; laboratory combined, about 1000/yr; commercial (five types), > 12,000/yr; and, commercial-laboratory, about 29,000/yr. It also manufactures electrodes as accessories for laboratory and commercial use (five types), 14,500/yr. All electrodes manufactured by this enterprise have the following pH range depending on the composition of the electrode glass: pH at 25°C from 0 to 12, working temperature from 0 to 40°C; pH from at 25°C 0 to 12, working temperature from 0 to 50°C; pH at 25°C from 0 to 14; working temperature from 25 to 100°C; pH at 25°C from 0.5 to 12 pH, working temperature from 20 to 60°C; pH at 80°C from 0 to 11, working temperature range from 70 to 150°C.

However, the chemical laboratories in manufacturing plants, industry and scientific-research institutes, and institutions of higher learning require glass electrodes which are stable against fluorine-containing and high-alkali media with pH ≥ 14. Only electrodes imported from, first and foremost, Germany (Jumo Company), meet this requirement.

The electrodes manufactured by GZIP are unstable in such media and rapidly fail, since the electrode glass used breaks down and rapidly loses the functions of an electrode. Unsatisfactory electrolytic keys are a considerable drawback of the glass electrodes manufactured; the keys are mechanically weak (strength < 2 MPa), the porosity is nonuniform (pore size 1 – 50 μm) and they do not provide a definite rate of outflow of the electrolyte.

The aim of the present work is to develop compositions and technological regimes for obtaining ceramic materials for electrolytic keys.

Electrolytic keys made from porous ceramic, which are actually miniature rods 1.2 ± 0.1 mm in diameter and 5 mm long and are used to fabricate glass reference electrodes, must meet a number of requirements. In the first place, they must allow glass blowing work associated with the fabrication of electrodes — soldering and vacuum-tight connections with tubes made from electrovacuum glass with linear thermal expansion coefficient CLTE = $(9.2 – 9.7) \times 10^{-6}$ K^{-1} (followed by firing in muffle furnaces). Ceramic keys must be chemically resistant to alkalis and acids, possess high mechanical strength ≥ 3 MPa, and uniform permeable porosity with pore size 1 – 5 μm, giving a rate of solution outflow to 3 ml/day. The electric resistance of a ceramic key at the boundary of two solutions must not exceed 10 – 15 kΩ. The key surfaces must be free of cracks, chipping, spalling, warping, and powder shedding from the surface [1].

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In order to ensure that the required specifications are met and strong welds with glass are obtained the ceramic must be synthesized on the basis of highly expanding crystalline phases (CLTE > 9.0×10^{-6} K^{-1}), whose number is quite limited, especially taking account of the required chemical stability against aggressive media, including fluoride solutions. According to the data of [2], crystalline phases with high CLTE include periclase, forsterite, cristobalite, quartz and their compositions with other phases. Compositions with the prescribed CLTE can be obtained by regulating the ratio of the crystalline phases in combination with the glass phase.

Porous ceramic for electrolytic keys with the prescribed properties can be obtained in the system Al_2O_3–SiO_2 (high-silica region) provided that cristobalite and a small number of other phases (quartz and mullite) crystallize. The chemical composition of the materials in the present system secures high chemical resistance to acid. The type and dispersity of the initial components have a large effect on the phase composition of the materials and their properties.

The conventional methods used in ceramic technology to obtain heat-insulating and filtering substances as well as foam- and gas-formation cannot be used to obtain a finely porous permeable structure of ceramic keys. These methods cannot give the uniform fine porosity required in electrolytic keys for slow filtering of a solution at a constant rate. This greatly limits the methods available for porization of a structure.

The following, experimentally determined, optimal chemical composition in the high-silica region of the system Al_2O_3–SiO_2 was chosen as the initial object for study (%[5]): 16.0 Al_2O_3 and 84.0 SiO_2 [3, 4]. Six ceramic mixes with the same chemical composition but different content of initial components were synthesized on its basis (%): refractory clay 30 – 50, quartz sand 40 – 65, amorphous silica 0 – 20 and bentonite 5 (> 100%).

Siliceous components were used to prepare the experimental mixes: quartz sand from the Dobrush Mineral Enrichment Combine (Gomel' Oblast', Belarus) and amorphous silica as well as a clayey component — Keramik-Vesko refractory clay from the Veselovskoe deposit (Ukraine).

A clay-containing component (above 100%) — bentonite from the Oglanlykskoe deposit — was used to ensure a mix with the plasticity required for obtaining ceramic keys by extrusion. This bentonite is a highly disperse montmorillonite rock, which increases the binding capacity of the molding paste. It actively participates in sintering and does not greatly affect the functional properties of the sintered product.

The preparation of the components and ceramic mixes and the synthesis of the experimental sample were all conducted using a technology that includes wet milling of the components, removing water from the slip and obtaining samples from the plastic paste by extrusion with a manually operated device.

The ceramic mixes were prepared by mixing and comminuting the components to a uniform batch by combined wet-milling a microball mill. The milling fineness was to residue ≤ 2 – 3% on a 0063 sieve. Next, the suspension was dried in a drying cabinet to moisture content 2 ± 1% and ground to a powder which was moistened to 16 – 18% (to a plastic state). Water removal to the required moisture content can be accomplished in gypsum molds. To homogenize the moisture content the mix was churned manually and allowed to cure for 2 – 3 days at constant moisture content. The experimental samples obtained by extrusion via a metal mold were fired at temperatures 1150, 1175 and 1200°C with soaking at maximum temperature 1 h.

The experimental samples of electrolytic keys fired at temperatures 1140, 1175 and 1200°C possessed water absorption 12 – 28%, porosity 22 – 52% and CLTE $(8.9 – 10.3) \times 10^{-6}$ K^{-1}.

Since it was established that the CLTE depends strongly on the form of the silica-containing component and the sintering temperature, the batch composition was adjusted for the small change in the ratio of the silica-containing components and plasticizing additives. The addition of refractory clay and bentonite as additives lowers the alkali sensitivity of the experimental samples and increases acid resistance by a very small amount; bentonite lowers the resistance to alkali media less than does clay, which is due to the difference of the chemical compositions of these components.

On the basis of a dilatometric analysis of the synthesized ceramic materials the experimental samples of electrolytic keys were picked according to the CLTE being close to that of electro-vacuum glass — $(9.2 – 11.1) \times 10^{-6}$ K^{-1} and transferred for tests to the Republic Unitary Enterprise Gomel' Instrumentation Works. Different glassblowers in the electrode section of the enterprise performed the work on ceramic keys in test tubes fabricated from corpus glass 360.

Different methods were used to seal the ceramic keys in a test tube made of glass 360: directly in the glass test tube and in an opening made in the test tube by a burner flame after the ceramic key was encapsulated in glass heated in a burner flame. It was determined that air is released when the ceramic keys are sealed in glass, but it is not necessary to release this air in the burner flame. This phenomenon was most easily observed for ceramic samples fired at lower temperatures. The gas release is probably due to the elevated porosity of ceramic materials or large pore size, which requires adjustments to the key preparation technology, i.e., changing batch fineness and the temperature-time firing regime used for the ceramic blanks.

Firing was conducted by two methods after the ceramic keys were sealed in the test tube: local firing in asbestos caps followed by firing in a muffle furnace at temperature 485 ± 5°C; after preparation the test tubes were placed in a muffle furnace heated to temperature 350 – 360°C, after which the temperature in the muffle furnace was raised to 485 ± 5°C and the test tubes were fire at this temperature.

A glass-ceramic junction must withstand sharp temperature differentials from 100 to 0°C as well as negative temperatures (to –25°C), so that after the test tubes with the sealed

[5] Here and below, the content by weight, wt.%.

TABLE 1. Batch Composition of Ceramic Mixes for the Experimental Samples

Component	Component content, wt.%, in composition		
	1	2	3
Keramik-Vesko clay from the Veselovskoe deposit	50	55	50
Quartz sand from the Dobrysh Mineral Enrichment Combine	40	40	45
Amorphous silica	10	5	5
Bentonite* from the Oglanlykskoe deposit	5	5	5

* Above 100%.

ceramic keys were fabricated tests were performed for thermal strength to check the integrity of the parts, including CLTE matching.

For the heat-resistance tests, the test tubes with the sealed ceramic were filled with a saturated solution of potassium chloride, placed in a vessel with distilled water, heated to 80 – 85°C and after a holding period transferred into water at temperature 15 – 20°C. The results showed that cracks appear at glass-ceramic junctions in some samples because the temperature dependences of the CLTE of the ceramic and electrovacuum glass were poorly matched.

It should be noted that the ceramic samples tested have the required CLTE in the range $(9.5 \pm 0.5) \times 10^{-6}\,K^{-1}$ at 400°C. The appearance of cracks in the glass-ceramic junction could be due to not only the difference in the CLTE values but also the different character of the temperature dependence of the CLTE. For joined materials with close values of the CLTE, as in the present case, cracks appear because of the second factor, i.e., different temperature dependence of the CLTE of the ceramic and glass.

The tests showed that the best heat-resistance obtains for a junction with a ceramic having the following composition: 50% refractory clay; 40% quartz sand; 10% amorphous silica; and, 5% bentonite (above 100%), fired at 1150°C. For this reason, in subsequent studies this composition was adjusted by varying the form and amount of its components without any significant changes in the chemical composition and the synthesis parameters for the ceramic (milling fineness, moisture content of the mix, amount of plasticizing agent and thixotropic hardening parameters) were determined.

Ceramic mixes based on the indicated composition, presented in Table 1, were prepared by combined wet milling in a microball mill for 1 h; the preceding samples were milled for 20 – 30 min. Increasing the milling time made it possible to increase the dispersity of the batch — the specific surface area increased from 5000 – 6000 to 7000 – 8500 cm^2/g. In turn, this will decrease the pore size in the material while preserving the overall porosity and it can be supposed that the gas release (i.e., the appearance of bubbles during soldering with glass) will decrease.

TABLE 2. Properties of Experimental Samples

Experimental composition	Porosity, %, samples fired at temperature, °C			
	total		open	
	1150	1200	1150	1200
1	63.0	61.2	50.8	48.78
2	66.0	59.4	46.6	45.7
3	66.0	63.3	52.5	45.2

Water was removed from the mix in a gypsum mold or by drying in a drying cabinet followed by rewetting to the require moisture content. The optimal moisture content of the mix, giving high-quality thin rods (electrolytic keys), was determined. Because of the higher dispersity of the mixture the optimal molding moisture content increased and was 20 ± 1%. It should be noted that the deviations of the moisture content from the optimal value should be minimal; otherwise, defects are unavoidable in the miniature blanks (voids, burrs, buckling and so forth).

The optimal conditions for thixotropic hardening of the paste required for plastic molding were determined. Curing the paste for 2 – 3 days at constant humidity and temperature 20 – 35°C is recommended. This will ensure active hydration of the clayey component and increase the strength of the plastic paste, which is extremely important for obtaining blanks by the extrusion method. Analysis of the experimental data showed that the optimal amount of plasticizing additive (bentonite) is 5%, while the optimal experimental mix compositions differed mainly by the ratio of the silica-containing components affecting the release of different polymorphic forms of crystalline silica and therefore the thermal expansion of the materials.

The dried experimental samples obtained by extrusion were fired in a charge of aluminum oxide in an electric furnace with temperature increasing in steps: increase to 300°C in 1 h with soaking for 30 min; 300 – 600°C in 1 h, 30 min soaking; 600 – 900°C in 1 h, 30 min soaking; 900°C to the maximum 1150 – 1200°C in 1 h, 60 min soaking.

As the experimental data show, after firing the experimental samples had a satisfactory exterior appearance with no deformation and burning.

The main characteristics of the experimental samples (water absorption, total and open porosity, temperature dependence of the relative elongation and CLTE in the temperature interval 20 – 600°C), as well as their physical composition and structure were studied. The results for the total and open porosity are presented in Table 2.

As one can see from the data in Table 2, the open porosity of the samples is 45.2 – 52.5% and depends mainly on the firing temperature.

Dilatometric analysis, presented in Fig. 1, shows that all experimental samples exhibit a nonlinear temperature dependence of the CLTE with a maximum at 200°C, which is

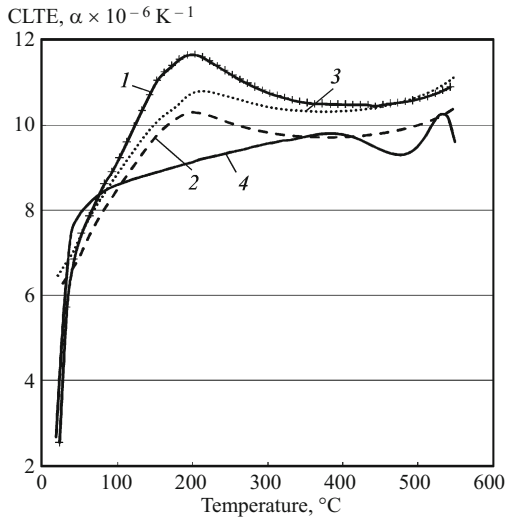

Fig. 1. Temperature dependence of the CLTE of experimental samples *1* – *3*, fired at temperature 1150°C, and the glass (*4*).

explained by the polymorphic transformation of cristobalite ($\beta \rightarrow \alpha$) [6], whose presence in a material is support by x-ray phase analysis, with volume increasing by about 3.5%.

In the temperature interval 20 – 600°C, the CLTE increases more in samples fired at 1200°C. This is due to an increase of the amount of cristobalite in the structure of the material as compared with quartz and mullite, which are also present; this is confirmed by an increase of the diffraction peaks in the x-ray diffraction patterns of the samples.

Comparing the CLTE of the samples as a function of the composition shows that the sample with composition No. 2 and crystal and amorphous silica ratio 8 : 1 and the maximum amount of clayey component possesses a flatter curve with the lowest extremum and with values closest to those for electrovacuum glass. At 400°C the CLTE of electrovacuum glass 360 is $9.79 \times 10^{-6}\ K^{-1}$, while for the ceramic sample CLTE = $9.72 \times 10^{-6}\ K^{-1}$.

The temperature dependences of the glass and ceramic CLTE presented in Fig. 1 differ somewhat: a trough is present in the curve for glass at 420 – 500°C, which is due to softening processes accompanied by volume changes. This specific feature of glassy materials distinguishes them from other inorganic materials, which must be taken into account when soldering with glass, depositing glassy coatings and performing other technological operations at high temperatures.

The phase composition of all experimental samples is identical and represented by quartz cristobalite and mullite. No significant differences in the phase composition as a function of the ratio of the components in the initial mixture are observed, but strong diffraction peaks of cristobalite are seen for composition No. 1 and the weakest peak for sample No. 2, which affects the thermal expansion of the materials (see Fig. 1). As temperature increases the intensity of the cristobalite precipitation increases considerably, since the thermodynamic probability of its formation increases. The

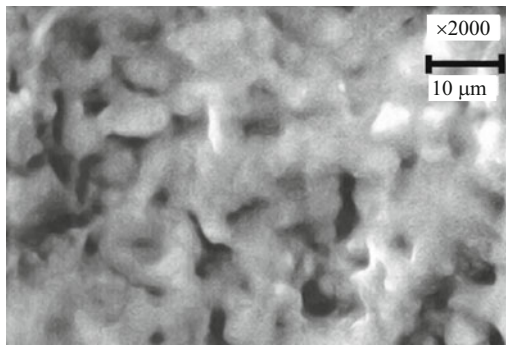

Fig. 2. Electron-microscope image of a cleavage surface of a sample with the optimal composition.

amount of quartz in the samples decreases in this case. The change of the phase composition is reflected in the temperature dependence of the CLTE: the maximum is more strongly expressed and the CLTE reaches $(14 – 15) \times 10^{-6}\ K^{-1}$, which can produce thermal stresses on soldering with glass.

The structure of the ceramic with optimal composition is characterized by a uniformly distributed porosity — the pore size fluctuates in the range 1 – 5 μm (Fig. 2).

Such porosity of the material is a necessary requirement for fabricating ceramic keys, since it can secure the required permeability and prescribed rate of solution outflow into the glass electrode.

A ceramic sample with the optimal composition with the ratio 8 : 1 of the crystalline and amorphous silica was chosen on the basis of the test results. The ceramic possesses the following physical-chemical indicators meeting the specifications for electrolytic keys: open porosity 45.4%, CLTE = $9.72 \times 10^{-6}\ K^{-1}$, mechanical strength 16 – 18 MPa, acid resistance 98% and specific resistivity $5 \times 10^{11}\ \Omega \cdot m$ at 500°C.

In summary, the new ceramic material with the optimal composition, containing a refractory clay as the plastic component and crystalline quartz (quartz sand) and amorphous silica (silica gel) in the ratio 8 : 1 as the silica-containing materials, possesses the required property set, which makes it suitable for the production of electrolytic keys for pH-measuring instruments.

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